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Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Sediment-Associated Biota: 1996 Revision

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# Toxicological Benchmarks for Screening Contaminants of Potential Concern for Effects on Sediment-Associated Biota: 1996 Revision

D. S. Jones R N. Hull G. W. Suter II

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Prepared by
Risk Assessment Program
Health Sciences Research Division
Oak Ridge, Tennessee 37831

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# LOCKHEED MARTIN ENERGY SYSTEMS, INC.

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## **AUTHOR AFFILIATIONS**

D. S. Jones and G. W. Suter II are members of the Environmental Sciences Division of Oak Ridge National Laboratory, Lockheed Martin Energy Research Corporation. R. H. Hull is currently affiliated with Beak Consultants Ltd., Brampton, Ontario.

#### **PREFACE**

The purpose of this report is to present sediment benchmark data and discuss their use as benchmarks for determining the level of toxicological effects on sediment-associated biota and to briefly describe three categories of approaches to the development of sediment quality benchmarks. This work was performed under Work Breakdown Structure 1.4.12.2.3.04.05.04 (Activity Data Sheet 8304, "Technical Integration—Risk Assessment"). Publication of this document meets a milestone for the Environmental Restoration (ER) Risk Assessment Program. This report is an update of a prior report (Hull and Suter, 1994). It contains an expanded list of National Oceanic and Atmospheric Administration and Ontario Ministry of the Environment values, an additional set of benchmarks from the Florida Department of Environmental Protection, an expanded list of benchmarks calculated for selected nonionic organic chemicals using equilibrium partitioning, and the U.S. Environmental Protection Agency Region IV and Office of Solid Waste and Emergency Response sediment screening values.

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#### **ACRONYMS**

AET apparent effects threshold

ARARs applicable or relevant and appropriate requirements

ASTM American Society for Testing and Materials

AVS acid volatile sulfide

CERCLA Comprehensive Environmental Response, Compensation, and Liability Act

DOC dissolved organic carbon

EPA U.S. Environmental Protection Agency

EqP equilibrium partitioning
ERA ecological risk assessment
ER-L Effects Range-Low
ER-M Effects Range-Median
ETs Ecotox Thresholds

FDEP Florida Department of Environmental Protection

f<sub>oc</sub> fraction organic carbon

 $K_{nc}$  organic carbon/water partition coefficient

 $K_{ow}$  octanol/water partition coefficient  $K_{p}$  sediment/water partition coefficient NAWQC National Ambient Water Quality Criteria

NOAA National Oceanic and Atmospheric Administration

OC organic carbon

OECD Organization for Economic Cooperation and Development

Ont. MOE Ontario Ministry of the Environment ORNL Oak Ridge National Laboratory

ORR Oak Ridge Reservation

OSWER Office of Solid Waste and Emergency Response

PAHs polycyclic aromatic hydrocarbons

**PCBs** polychlorinated biphenyls **PELs** Probable Effects Levels PQL **Practical Quantitation Limit SEM** simultaneously extracted metal SLC screening level concentration SOB sediment quality benchmark SQC sediment quality criterion sediment quality guideline SOG

SSLC species screening level concentration

SVs screening values

TELs Threshold Effects Levels

TIE toxicity identification evaluation

TOC total organic carbon

WI DNR Wisconsin Department of Natural Resources

WQB water quality benchmark WQC water quality criteria

#### **EXECUTIVE SUMMARY**

A hazardous waste site may contain hundreds of chemicals; therefore, it is important to screen contaminants of potential concern for the ecological risk assessment. Often this screening is done as part of a Screening Assessment, the purpose of which is to evaluate the available data, identify data gaps, and screen contaminants of potential concern. Screening may be accomplished by using a set of toxicological benchmarks. These benchmarks are helpful in determining whether contaminants warrant further assessment or are at a level that requires no further attention. If a chemical concentration or the reported detection limit exceeds a proposed lower benchmark, more analysis is needed to determine the hazards posed by that chemical. If, however, the chemical concentration falls below the lower benchmark value, the chemical may be eliminated from further study.

This report briefly describes three categories of approaches to the development of sediment quality benchmarks. These approaches are based on analytical chemistry, toxicity test results, and field survey data. A fourth integrative approach incorporates all three types of data.

The use of multiple benchmarks is recommended for screening chemicals of concern in sediments. Equilibrium partitioning benchmarks are included for screening nonionic organic chemicals. Field survey benchmarks developed for the Ontario Ministry of the Environment (Ont. MOE) are included for inorganic and organic chemicals. Integrative benchmarks developed for the National Oceanic and Atmospheric Administration (NOAA) and the Florida Department of Environmental Protection (FDEP) are included for inorganic and organic chemicals. In addition, U.S. Environmental Protection Agency (EPA) sediment quality criteria are included along with screening values from EPA Region IV and ecotox threshold values from the EPA Office of Solid Waste and Emergency Response (OSWER). Pore water analysis is recommended for ionic organic compounds; comparisons are then made against water quality benchmarks.

This report is an update of a prior report (Hull and Suter 1994). It contains an expanded list of NOAA and Ont. MOE values, an additional set of benchmarks from the FDEP, an expanded list of benchmarks calculated for selected nonionic organic chemicals using equilibrium partitioning, and EPA Region IV and OSWER sediment screening values.

#### 1. INTRODUCTION

A hazardous waste site may contain hundreds of chemicals; therefore, it is important to screen contaminants of potential concern for the ecological risk assessment (ERA). Often this screening is done as part of a Screening Assessment, the purpose of which is to evaluate the available data, identify data gaps, and screen contaminants of potential concern. Screening may be accomplished by using a set of toxicological benchmarks. These benchmarks are helpful in determining whether contaminants warrant further assessment or are at a level that requires no further attention. If a chemical concentration or the reported detection limit exceeds a lower benchmark, more analysis is needed to determine the hazards posed by that chemical. If, however, the chemical concentration falls below the lower benchmark value, the chemical may be eliminated from further study. Concentrations exceeding an upper screening benchmark indicate that the chemical in question is clearly of concern and that remedial actions are likely to be needed.

The use of multiple benchmarks also provides an indication of the likelihood and nature of effects. For example, exceedance of only one conservatively estimated benchmark may provide weak evidence of real effects, whereas exceedance of multiple benchmarks of varying conservatism may provide strong evidence of real effects. Likewise, if a nonionic organic chemical only exceeds benchmarks that are not normalized to site-specific organic carbon content, then organisms that ingest sediment may be more exposed than those that do not. These inferences can be used to refine future sampling and remediation efforts.

In recent years, protecting sediment quality has been viewed as a logical and needed extension of water quality protection (Adams et al. 1992). The U.S. Environmental Protection Agency (EPA) is authorized to develop and implement sediment quality criteria (SQC) under Section 304(a) of the Clean Water Act (EPA 1989a). EPA released five SQC documents in 1993 (EPA 1993a to e). In addition, EPA Region IV (1995) and the Office of Solid Waste and Emergency Response (OSWER) (1996) released sediment screening values in 1995. Until EPA's task is complete, efforts will continue around the United States and abroad (MacDonald 1993, Persaud et al. 1990) to develop SQC and benchmark values for the assessment of sediment quality at hazardous waste sites.

Sediment quality benchmarks (SQBs) are necessary, in addition to water quality benchmarks (WQBs), because (1) various toxic contaminants found in only trace amounts in the water column accumulate in sediments to elevated levels; (2) sediments serve as both a reservoir and a source of contaminants to the water column; (3) sediments integrate contaminant concentrations over time, whereas water column contaminant concentrations are much more variable and dynamic; (4) sediment contaminants in addition to water column contaminants affect benthic and other sediment-associated organisms; and (5) sediments are an integral part of the aquatic environment, providing habitat, feeding, and rearing areas for many aquatic organisms (Chapman 1989).

To make decisions as to whether a chemical or biological measurement of sediment quality indicates impairment, site-specific data may be compared with benchmarks that indicate whether sediment quality is acceptable. Existing criteria and standards are considered a type of benchmark. The purpose of this report is to present sediment benchmark data and discuss their use as benchmarks for determining the level of toxicological effects on sediment-associated biota.

It is important to note, however, that these benchmarks do not represent remediation goals. Remediation goals must consider adverse effects on habitat and remobilization of contaminants caused by removal or remediation of sediments.

The benchmarks in this report are to be used at the U.S. Department of Energy's (DOE's) Oak Ridge Reservation (ORR) and at the Portsmouth and Paducah Gaseous Diffusion plants as screening values only to show the nature and extent of contamination and identify the need for additional site-specific investigation (e.g., biological and chemical testing).

Sediment benchmarks also can be used for baseline ERAs, which are required under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) at Superfund sites. These assessments evaluate the risks to the environment posed by the hazardous waste site. Sediment benchmarks must not be used as the sole measure of sediment toxicity. Field studies and toxicity tests shall be the primary indicators of toxicity of sediments; benchmarks may be used to determine which chemicals present in the sediment are most likely causing the toxicity. This integrative approach allows a more accurate evaluation of adverse ecological impact, which is necessary in a baseline risk assessment.

This report is an update of a prior report (Hull and Suter, 1994). It contains an expanded list of Effects Range-Low (ER-L), Effects Range-Median (ER-M), and Ontario Ministry of the Environment (Ont. MOE) values; an additional set of benchmarks from the Florida Department of Environmental Protection (FDEP); an expanded list of benchmarks calculated for selected nonionic organic chemicals using equilibrium partitioning; the Reg IV and OSWER sediment screening values; and the five EPA sediment quality criteria.

# 2. REVIEW OF POSSIBLE APPROACHES TO BENCHMARK DEVELOPMENT

Three distinct categories of approaches can be used in the development of SQBs. These approaches are based on analytical chemistry, toxicity test results, and field survey data. A fourth integrative approach incorporates all three types of data. Regardless of the method, a numeric benchmark results.

The scientific and regulatory communities are still debating the best methods to be used to develop sediment quality guidelines. This diversity of opinion is demonstrated by the wide variety of methods being studied and by the fact that the state of Washington has implemented sediment quality standards based on the apparent effects threshold (AET) approach, whereas the equilibrium partitioning (EqP) approach is favored by the EPA Office of Water and Regulations (Adams et al. 1992). The Organization for Economic Cooperation and Development (OECD 1992) released a report on effects assessment of chemicals in sediment; this report evaluates eight methods for developing sediment quality objectives. Based on the evaluation criteria outlined in the report, three methods were recommended for deriving sediment quality objectives: the EqP approach, the measurement of interstitial water, and spiked sediment toxicity tests.

Several of the possible approaches to developing SQBs are described in the following sections. The various methods have been reviewed (Adams et al. 1992, MacDonald et al. 1992, MacDonald 1994, Chapman 1989). A summary of some of the advantages and disadvantages of each of these approaches is given in Tables 1 and 2.

Table 1. Summary of advantages of the various approaches to the development of SQBs<sup>a</sup>

Approach	Simple	Useful for metal toxicity	Uses existing WQC <sup>a</sup>	Accepted methods	Used with any chemical	Combined chemical effects determined	Effects- based
Background	x			x			
Pore water		x	X				x
$\operatorname{EqP}^a$			x	x			x
AVS <sup>a</sup>		x		X			x
Toxicity tests					X	X	x
$SLC^a$		X		X	x		x
AET <sup>a</sup>		x		х.	x	x	x
Triad		x			X	x	x
NOAA <sup>a</sup>	x	x		X	X		x
$FDEP^a$	х	x		X	x		x

<sup>&</sup>lt;sup>a</sup>SQBs = sediment quality benchmarks; WQC = water quality criterion; EqP = equilibrium partitioning; AVS = acid volatile sulfide; SLC = screening level concentration; AET = apparent effects threshold; NOAA = National Oceanic and Atmospheric Administration; FDEP = Florida Department of the Environment.

Table 2. Summary of disadvantages of the various approaches to the development of SQBs<sup>a</sup>

Approach	Site- specific	No biological basis	Inorganics only	Nonionic organics only	Large field effort required	Cannot distinguish between one and several chemicals	Cannot be used for synthetic organics	Missing standard methods	Sampling may alter toxicity
Background		x					X		
Pore water								x	x
$\operatorname{EqP}^a$				x					
AVS <sup>a</sup>			x				X		
Toxicity tests					X	X		X	X
$SLC^a$					X	· <b>x</b>			
AET <sup>a</sup>	x			•	X	X			
Triad					x			x	
NOAA <sup>a</sup>						X			
$FDEP^a$						X			

<sup>&</sup>lt;sup>a</sup>SQBs = sediment quality benchmarks; EqP = equilibrium partitioning; AVS = acid volatile sulfide; SLC = screening level concentration; AET = apparent effects threshold; NOAA = National Oceanic and Atmospheric Administration; FDEP = Florida Department of Environmental Protection..

#### 2.1 ANALYTICAL CHEMISTRY APPROACHES

#### 2.1.1 Water Quality Benchmark Approaches

#### 2.1.1.1 Direct measurement of interstitial water

The direct measurement of interstitial water approach compares the concentrations of contaminants in sediment interstitial (pore) waters with the EPA water quality criteria (WQC) (EPA 1993f) and other WQBs. WQBs of varying conservatism have been developed at Oak Ridge National Laboratory (ORNL) (Suter and Tsao 1996) because many chemicals do not have national ambient WQC. Maughan (1993) suggests that the analysis of sediment pore water is a more appropriate method for screening than using bulk sediment chemistry. He cites the advantages of the flexibility and acceptance of pore water testing.

It can be argued that benthic organisms are exposed to contaminants via other exposure routes, such as dermal absorption and ingestion of sediment particles. An analysis of freshwater benthic species' feeding habits concluded that these species were not sediment ingesters, with the exception of the oligochaetes (aquatic earthworms) and some chironomids that are both filter feeders and occasional sediment ingesters (Adams 1987). In contrast to this, marine burrowing species frequently ingest sediment (Adams 1987). For the clam *Macoma nasuta*, uptake of highly lipophilic pollutants occurred primarily by ingestion of solids (63 to 84%), followed by ventilation of interstitial water across the gills (11 to 12%) (Boese et al. 1990). This may be because *Macoma nasuta* predominantly ventilates overlying water, not interstitial water.

Such discrimination between overlying and interstitial water also may be important for tube dwellers (e.g., chironomids and hexagenia) that pump overlying water through their burrows (Landrum and Robbins 1990). Maughan (1993) argues that if the organism is in equilibrium with the pore water, then the concentration in the pore water would reflect the sum of all exposure routes. Therefore, an organism that has accumulated contaminants, through feeding, at a higher concentration than the equilibrium with pore water would re-establish the equilibrium by losing contaminants to the pore water (Maughan 1993). However, factors may influence whether the organism can establish an equilibrium with the pore water. For example, diffusion within the interstitial water may limit transfer of desorbed compounds to the organism (Landrum and Robbins 1990).

Direct measurement of pore water would yield useful information for contaminants lacking bulk sediment contaminant benchmarks (e.g., ionic organics). However, this is not recommended if estimation of the pore water concentration can be done using the EqP approach for reasons explained in the following text.

# 2.1.1.2 Estimation of interstitial water concentrations: sediment/water equilibrium partitioning approach

Nonionic organics. This approach calculates a bulk sediment chemical concentration benchmark. The calculation uses the WQBs together with correction factors for the effects of organic carbon (OC) (EPA 1993f).

An SQB using this method is calculated as follows (EPA 1993f): If the WQB (micrograms per liter) is a water quality benchmark for the chemical of interest (Suter and Tsao 1996), then the SQB (micrograms per kilogram sediment) is computed using the partition coefficient  $K_p$  (liters per kilogram sediment) between sediment and water:

$$SQB = K_p \times WQB$$
.

The partitioning of nonionic chemicals between particles and water depends on the partition coefficient  $K_{oc}$  for the particles' OC and the mass fraction of OC ( $f_{oc}$ ; kilograms OC per kilogram sediment) of the particles:

$$K_p = f_{oc} \times K_{oc}$$
.

Where the  $K_{oc}$  is unavailable, it is estimated by the octanol-water partition coefficient  $K_{ow}$  of the chemical for sediments using the following equation (Di Toro 1985):

$$\log_{10}(K_{oc})=0.0028+0.983 \log_{10}(K_{ow}).$$

Therefore,

$$SQB = f_{oc} \times K_{oc} \times WQB$$
.

The EqP approach makes major four assumptions: (1) partitioning of the organic chemical between organic carbon and interstitial water is stable at equilibrium; (2) the sensitivities of benthic species and species tested to derive WQC, predominantly water column species, are similar; (3) the levels of protection afforded by WQC are appropriate for benthic organisms; and (4) exposures are similar regardless of feeding type or habitat (EPA 1993a).

EqP can be used only if  $f_{\infty} > 0.2\%$ . At  $f_{\infty} < 0.2\%$ , the factors controlling second-order effects on partitioning (e.g., particle size, sorption to nonorganic mineral fractions) become relatively more important (EPA 1993f).

For both the direct measurement and EqP approaches for estimating pore water effects concentrations, it is assumed that the WQBs, when applied to the interstitial water of sediments, would protect infaunal organisms. EPA (1993f) has concluded that the sensitivities of benthic species are sufficiently similar to those of water column species to tentatively permit the use of WQBs for the derivation of SQBs.

The EqP approach is favored by the EPA over the direct measuring of pore water approach (EPA 1993f). The free chemical concentration in pore water can be estimated directly from the OC normalized sediment concentration, and the estimate is independent of the dissolved organic carbon (DOC) concentration. Using the pore water chemical concentration to estimate the free pore water chemical concentration requires that the DOC concentration and the DOC partition coefficient be known; this is because the proportion of a chemical in pore water that is complexed to DOC can be substantial. However, it is the free, uncomplexed component that is bioavailable and that is in equilibrium with the OC normalized sediment concentration. Therefore, for highly hydrophobic chemicals and where there is significant DOC complexing, the solid-phase chemical concentration gives a more direct estimate of the bioavailable pore water contaminant concentration than do the pore water concentrations (EPA 1993f).

Metals: equilibrium partitioning approach. Significant complexities are associated with inorganic chemicals when using the EqP approach. Uptake (and therefore effects) of sediment-associated contaminants is largely a function of bioavailability. Bioavailability is strongly influenced by a complex suite of physical, chemical, and biological factors in the sediments. Trace metals can be adsorbed at particle surfaces, bound to carbonates, occluded in iron and/or manganese oxyhydroxides, bound to organic matter, bound to sulphide, bound to a matrix, or dissolved in the interstitial water. The complexity of trace metal bioavailability associated with these phases hinders the prediction of effects (Campbell and Tessier 1991). For these reasons, the EqP approach is not recommended for screening metals.

Metals: acid volatile sulfide method. Acid volatile sulfide (AVS) is a reactive pool of solid-phase sulfide that is available to bind metals and render that portion unavailable and nontoxic to biota (Di Toro et al. 1992). The AVS is extracted from sediment using hydrochloric acid. The metal concentration that is simultaneously extracted is termed the simultaneously extracted metal (SEM). For [SEM]/[AVS] <1, no acute toxicity (mortality >50%) has been observed in any sediment for any benthic test organism. For [SEM]/[AVS] >1, less sensitive organisms can tolerate increased metal activity. However, the mortality of sensitive species (e.g., amphipods) increases in the range of 1.5 to 2.5 μmol of SEM/μmol of AVS (Di Toro et al. 1992). For this reason, the AVS method is used only to predict when a sediment in not acutely toxic.

The AVS approach requires the measurement of all toxic SEMs that are present in amounts that would contribute significantly to the SEM sum. Failure to do so could lead to an incorrect conclusion of lack of acute toxicity (Di Toro et al. 1992). Use of the AVS method would be invalid if the sediment AVS content is very low. This would occur in fully oxidized sediments (Adams et al. 1992). In addition, only five metals (Cd, Cu, Pb, Ni, and Zn) currently can be evaluated using AVS (EPA 1994), and the AVS method has not been adapted for chronic toxicity.

The AVS method is seldom applicable to screening risk assessments because the needed data are not available. It is usually not recommended for baseline risk assessments because its validity is not generally accepted.

#### 2.2 SEDIMENT TOXICITY TEST APPROACHES

#### 2.2.1 Bulk Sediment Toxicity Tests

Organisms are exposed to either contaminated field-collected sediments or background sediments spiked in the laboratory with known amounts of single chemicals or mixtures. Mortality or sublethal effects are observed, and dose-response relationships are determined (Chapman 1989, Long and Morgan 1991). A major advantage to this approach is that it follows the methods used to develop WQC; therefore, the procedure and rationale are technically acceptable and legally defensible (Chapman 1989). The use of sediment toxicity tests has become firmly entrenched in many dredged material permitting and benthic survey programs (Burton and Scott 1992). Several disadvantages include: toxicity tests do not provide chemical-specific benchmarks, toxicity test methods have yet to be standardized, and toxicity tests may not reflect chronic effects (Chapman 1989).

This approach is too costly and labor intensive for screening purposes, and frequently the data are not available. It is recommended that bulk sediment toxicity tests be incorporated into a baseline ERA sampling and analysis plan.

#### 2.2.2 Pore Water Toxicity Tests.

Sediment pore water can be used in standardized toxicity tests, and toxicity identification evaluation (TIE) procedures can be used to characterize, identify, and then confirm the toxic components of a complex aqueous solution. However, TIE procedures may be difficult and costly (Maughan 1993). Currently, no universally accepted method for extracting pore water from sediment exists. In addition, pore water is difficult to extract from sediment without potentially altering the toxicity of the pore water (Maughan 1993).

Pore water toxicity tests could be incorporated into screening and baseline ERAs if bulk sediment toxicity tests cannot be used.

#### 2.3 FIELD SURVEY APPROACHES

#### 2.3.1 Screening Level Concentration Approach

The screening level concentration (SLC) approach estimates the highest concentration of a particular contaminant in sediment that can be tolerated by ~95% of benthic infauna (Neff et al. 1988). The SLC is derived from synoptic data on sediment chemical concentrations and benthic invertebrate distributions. First, the species screening level concentration (SSLC) is calculated by plotting the frequency distribution of the contaminant concentrations over all sites (at least 10) where the species is present. The 90th percentile of this distribution is taken as the SSLC for that species. Next, a large number of SSLCs are plotted as a frequency distribution to determine the contaminant concentration above which 95% of the SSLCs occur. This final concentration is the SLC (Neff et al. 1988).

The SLC approach has several advantages: it can be used with any chemical contaminant, it can be developed using existing data bases and methodologies, and it does not require a priori assumptions concerning mechanisms of interaction between organisms and toxic contaminants (Chapman 1989). Disadvantages include: a large amount of field data is required, a precise level of infaunal taxonomic identification is required, calculation of SLCs is affected by the range and distribution of contaminant concentrations and species, selection criteria for species have not been established, and no mechanism has been established to separate single contaminant effects from the effects of all contaminants combined (Chapman 1989).

The SLC method is not recommended for benchmark development. However, existing SLC values can be used in the screening of contaminants of potential concern.

#### 2.3.2 Apparent Effects Threshold Approach

The AET approach uses data from matched sediment chemistry and biological effects measures. Biological effects could be assessed by either benthic community survey or sediment toxicity tests. An AET concentration is the sediment concentration of a selected chemical above which statistically significant biological effects always occur (EPA 1989b).

The major strengths of the approach are (1) combined chemical effects can be considered (EPA 1989b); (2) there are no constraints on the type of contaminant or biological effects that can be used; (3) contaminants that are most likely associated with observed biological effects are identified on a site-specific basis; and (4) because observed biological effects always occur above the AET, the approach provides values based on noncontradictory evidence of biological impacts (Chapman 1989).

Disadvantages to this approach include: (1) it is site-specific (EPA 1989b), (2) it may be under protective maintenance because biological effects are observed at chemical concentrations well below AET values, (3) it requires a large data base for chemical variables and at least one biological indicator, and (4) combined contaminant effects cannot be separated from single contaminant effects (Chapman 1989).

The AET approach is not recommended for benchmark development. However, existing AET values can be used in the screening of contaminants of potential concern.

#### 2.4 INTEGRATIVE APPROACHES

#### 2.4.1 Sediment Quality Triad

The sediment quality triad approach is based on correspondences between three measures: sediment chemistry to determine contamination, sediment toxicity tests to determine toxicity, and in situ bioeffects (e.g., benthic infaunal community structure) to determine alteration of resident communities (Chapman 1989). Table 3 describes the information provided by various responses to these three measures.

The major advantage of the triad approach is that the combination of the three separate measures in a weight-of-evidence approach allows for differentiation of toxicity related to contamination from natural variability and/or laboratory artifacts (Chapman 1989). The approach incorporates interactions between contaminants in complex sediment mixtures, including additivity, antagonism, and synergism; actions of unidentified toxic chemicals; and effects of environmental factors that influence biological responses. A major disadvantage is that this method is both labor intensive and expensive (Chapman et al. 1992).

An integrative approach is required for a technically complete baseline ERA, especially at a large waste site with numerous contaminants in several media and where there are potentially several exposure pathways. This approach is pursued for baseline ERAs at DOE sites, such as the ORR (Suter et al. 1995). Although the full triad of sediment data is not available for screening assessments, the weight of evidence should be considered whenever multiple measures are available.

#### 2.4.2 National Oceanic and Atmospheric Administration Approach

Because the EqP approach is impractical for inorganics, other benchmark values were needed. EPA Region IV (1995) and OSWER (1996) have recommended the National Oceanic and Atmospheric Administration (NOAA) methodology for screening inorganic and organic chemicals at waste sites. NOAA annually collects and chemically analyzes sediment samples from sites located in coastal marine and estuarine environments throughout the United States. These data were used to evaluate three basic approaches to the establishment of effects-based criteria: the EqP approach, the spiked-sediment toxicity test approach, and various methods of evaluating synoptically collected biological and chemical data in field surveys (Long and Morgan 1991). Chemical concentrations observed or predicted by these methods to be associated with biological effects were ranked, and the lower 10th percentile [Effects Range-Low (ER-L)] and median [Effects Range-Median (ER-M)] concentrations were identified.

Table 3. Information provided by differential sediment quality triad responses<sup>a</sup>

Situation	Chemicals present	Toxicity	Alteration	Possible conclusions
1	+	+	+	Strong evidence for pollution-induced degradation
2		-	-	Strong evidence that there is no pollution-induced degradation
3	+	-	-	Contaminants are not bioavailable or are present at nontoxic levels
4	-	+	-	Unmeasured chemicals or conditions exist with the potential to cause degradation
5	-	-	+	Alteration is not due to toxic chemicals
6	+	+	-	Toxic chemicals are stressing the system
7	-	+	+	Unmeasured toxic chemicals are causing degradation
8	+	_	+	Toxicity tests are insufficiently sensitive or alteration is not due to toxic chemicals

<sup>&</sup>lt;sup>a</sup>Responses are shown as either positive (+) or negative (-), indicating whether or not measurable (e.g., statistically significant) differences from control/reference conditions/measures are determined.

Source: Chapman, P. M. 1990. The Sediment Quality Triad Approach to Determining Pollution-Induced Degradation. Sci. Total Environ. 97/98, 815-825.

The ER-L and ER-M values were recalculated by Long et al. (1995) after omitting the few freshwater data included in the Long and Morgan (1991) calculations and after adding additional, more recent data. These revised ER-L and ER-M values are recommended for screening contaminants of potential concern.

#### 2.4.3 Florida Department of Environmental Protection Approach

The Florida Department of Environmental Protection (FDEP) approach (MacDonald 1994) is similar to the NOAA approach. The updated and revised data set used by Long et al. (1995) also was used by MacDonald (1994) to calculate Threshold Effects Levels (TELs) and Probable Effects Levels (PELs); these data are presented by MacDonald et al. (1994). However, unlike the ER-Ls and ER-Ms, the TELs and PELs also incorporate chemical concentrations observed or predicted to be associated with no adverse biological effects (no effects data). Specifically, the TEL is the geometric mean of the 15th percentile in the effects data set and the 50th percentile in the no effects data set. The PEL is the geometric mean of the 50th percentile in the effects data set and the 85th percentile in the no effects data set. Therefore, the TEL represents the upper limit of the range of sediment contaminant concentrations dominated by no effects data. The PEL represents the lower limit of the range of contaminant concentrations that are usually or always associated with adverse biological effects (MacDonald 1994).

EPA Region IV (1995) also has recommended the FDEP methodology for establishing potential sediment screening values. TELs and PELs are recommended for screening chemicals of potential concern.

#### 2.5 BACKGROUND CONCENTRATIONS

Comparison of site contaminant levels with background levels is a simple screening method. The assumption is that concentrations that are not higher than background are not hazardous. Appropriate background samples must be obtained for waste site samples. The American Society for Testing and Materials (ASTM) is currently developing guidelines for selection of sediment and soil background sampling locations (ASTM Section E47.13.01, Task E).

This approach has two major disadvantages: it has no biological effects basis, and it cannot be used for synthetic organic compounds, which should not be present in background sediments. Therefore, this approach should not be used as the only screening method. It is appropriate to use the background concentrations to screen the other sediment benchmarks. Sediment benchmarks that are below background contaminant concentrations are not retained as benchmarks when screening site sediments.

#### 3. RECOMMENDED SEDIMENT BENCHMARKS

The following section presents the recommended sediment benchmarks for use at DOE's ORR and at the Portsmouth and Paducah Gaseous Diffusion plants. The rationale, interpretation, and general considerations for their use in screening sediment chemical data also are briefly discussed. Chemical-specific considerations are presented in Sect. 4.

This revision includes an expanded suite of sediment benchmarks, including new benchmarks (e.g., FDEP TELs and PELs and EPA screening values) and additional chemicals for previously presented benchmarks (e.g., ER-Ls and ER-Ms for organic chemicals). The use of multiple benchmarks of varying conservatism is recommended to provide a robust evaluation of the chemical data. That is, a suite of benchmarks reduces the chances of missing a chemical of potential ecological concern and increases the interpretive value of the chemical data set. Three benchmarks included in the previous version (Hull and Suter 1994) are not included in this revision. They were poorly founded scientifically and only considered suitable for evaluating dredged sediments for open water disposal (EPA Region V values), derived using the background methodology (WADOE and BEAK), and did not appreciably add to the interpretive power of the suite of benchmarks.

It is strongly recommended that the suite of benchmarks be explicitly included in the Data Quality Objectives process to get early and informed regulator agreement for their use in a given project.

#### 3.1 EQUILIBRIUM PARTITIONING BENCHMARKS

The EPA has chosen the EqP approach for developing SQC for nonionic organics (EPA 1993f). This is also a methodology that ORNL supports for developing SQBs when bulk sediment concentrations and WQBs are available.

The EqP approach requires a WQB, a K<sub>oc</sub> value, and a measured or assumed site-specific total organic carbon (TOC) value. Because many chemicals do not have National Ambient Water Quality Criteria (NAWQC), sets of WQBs of varying conservatism have been developed at ORNL (Suter and Tsao 1996). Consult this publication, or its most recent revision, for a complete discussion of the aquatic benchmarks and their uses. Secondary chronic values are intended to be conservative predictors of effects. If concentrations exceed benchmarks that used the NAWQC, the chemicals must be contaminants of concern because the NAWQC are applicable or relevant and appropriate requirements (ARARs). Concentrations that exceed Lowest Chronic Value benchmarks indicate a risk of real effects. Table 4 lists the available log K<sub>ow</sub> values for selected nonionic organic contaminants, the sources of these values, the calculated log K<sub>ow</sub> values, and the estimated SQBs corresponding to the conventional aqueous benchmarks; these SQBs are normalized assuming 1% TOC.

For polar organic chemicals, adsorption mechanisms other than hydrophobicity may significantly increase the fraction of the chemical sorbed to the sediment particles (EPA 1993f). Therefore, the  $K_{\infty}$ -based model is likely to overestimate the free, and therefore bioavailable, chemical concentration. SQBs for selected polar nonionic organic chemicals are included in Table 4 as conservative benchmarks and are denoted appropriately.

The bulk sediment contaminant concentrations measured at a site can be compared directly to the SQBs presented in Table 4. It is recommended, however, that these benchmarks be adjusted by multiplying the SBQ by the site-specific percent TOC. For example, the SQC for acenaphthene is  $1300 \mu g/kg$  assuming 1% TOC and  $13,000 \mu g/kg$  assuming 10% TOC (EPA 1993a). However, the EqP methodology, and therefore these benchmarks, is not appropriate for sediments with less than 0.2% TOC (EPA 1993f).

#### 3.2 INTEGRATIVE BENCHMARKS

EPA Region IV (1995) has recommended the NOAA and FDEP values as potential lower screening values, and EPA OSWER (1996) has recommended the NOAA values as potential ecotoxicological threshold values. The NOAA and FDEP values also are supported by ORNL as SQBs when bulk sediment chemical concentrations are available.

The data compiled by MacDonald et al. (1994) are from marine and estuarine locations only. The use of the NOAA and FDEP values for freshwater is appropriate in the absence of reliable freshwater sediment benchmarks. Klapow and Lewis (1979) investigated the question of whether or not it was legitimate to combine freshwater and marine aqueous toxicity data to develop marine water quality benchmarks. A statistical test of medians was applied to freshwater and marine acute toxicity data for nine metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn) and non-chlorinated phenolic compounds. In only one case (Cd) was there a statistically significant difference in the median response of marine and freshwater organisms. The NOAA and FDEP values were developed from data from several investigations throughout the United States, and these studies used different approaches to evaluate sediment quality (e.g., toxicity tests, EqP, AET). It is assumed that the use of numerous data and the calculation of percentiles help eliminate the influence of a single (possibly outlier) data point, thereby making the sediment quality values more credible (Long and Morgan 1991).

The NOAA values may be used to help identify sites with the potential to cause adverse biological effects. These are not NOAA criteria or standards and are not intended for use in regulatory decisions or any other similar applications (Long and Morgan 1991).

Table 4. Summary of EqP-derived sediment quality benchmarks, for nonionic organic chemicals, corresponding to conventional aqueous benchmarks

					L	owest Chronic Value i	or:
Chemical	Log Kow <sup>b</sup>	Log Koc	NAWQC Chronic	Secondary Chronic Value	Fish	Daphuids	Non-Daphnid Invertebrates
Acenaphthene	3.92	3.86	1300°		5314	477,222	16,300
Acetoned	-0.24	-0.23		8.77	2968	9.12	
Anthracene	4.55	4.48		218	26.9	<628	
Benzene	2.13	2.10		162		>122,4100	:
Benzidine <sup>d</sup>	1.66	1.63		1.68	57.8		
Benzo(a)anthracene	5.70	5.61		109		2623	:
Benzo(a)pyrene	6.11	6.01		143		3062	
Benzyl alcohold	1.11	1.09		1.07	73.1		ţ
BHC (lindane)	3.73	3.67	3.74		682	677	154
BHC (other)	3.80°	3.74		120		5199	
Biphenyl	3.96 <sup>r</sup>	3.90		1100			
Bis(2-ethylhexyl)phthalate	7.60 <b>°</b>	7.47	892,732				
4-Bromophenyl phenyl ether	5.00	4.92		1241			
Butylbenzyl phthalate	4.84	4.76		10,946			ı
2-Butanone <sup>4</sup>	0.29*	0.29		271	5475	27,066	
Carbon disulfide	2.00	1.97		0.856	8877	227	
Carbon tetrachloride	2.73	2.69		47.6	9569	27,103	
Chlordane	6.32	6.22	2790		26,271	262,712	17,897
Chlorobenzene	2.86	2.81		417	7842	98,059	
Chloroform	1.92	1.89		99.4	963	3481	

Table 4. (continued)

	Chronic		1	Lowest Chronic Value	for:		
Chemical		Log Koc		Secondary Chronic Value -	Fish	Daphnids	Non-Daphnid Invertebrates
p,p'-DDD	6.10	6.00		110	16,865		
DDT	6.53	6.42		343 <sup>bf</sup>	19,280	422	
Decane	5.01 <sup>s</sup>	4.93		41,478		6,665,388	
Di-n-butyl phthalate	4.61	4.53		11,981	254,442	238,596	•
Diazinon	3.70 <sup>r</sup>	3.64		1.88			
Dibenzofuran	4.12 <sup>8</sup>	4.05		418		113,256	
1,2-Dichlorobenzene	3.43	3.37		332			·
1,3-Dichlorobenzene	3.43 <sup>t</sup>	3.37		1682			,
1,4-Dichlorobenzene	3.42	3.36		347			
1,1-Dichloroethane	1.79	1.76		27.2	8494		
1,2-Dichloroethane	1.47	1.45		255	11,599	4262	
1,1-Dichloroethene	2.13	2.10		31.2	>3497	5896	
1,2-Dichloroethene	1.86°	1.83		400	6466		
1,3-Dichloropropene	2.00	1.97		0.0512	227	749	
Dieldrin	5.37	5.28	110°				
Diethyl phthalate	2.50	2.46		606			
Endosulfan, all isomers	4.10	4.03		5.50			
Endrin	5.06	4.98	42°				
Ethyl benzene	3.14	3.09		89.7	>5406	158,763	
Fluoranthene	5.12	5.04	6200°		32,575	16,287	

Table 4. (continued)

					1	Lowest Chronic Value	for:
Chemical	Log Kow <sup>b</sup>		NAWQC Chronic	Secondary Chronic Value	Fish	Daphnids	Non-Daphnid Invertebrates
Fluorene	4.21	4.14		540			
Heptachlor	6.10 <sup>s</sup>	6.00		68.8	12,574	31,734	
Hexachloroethane	4.00	3.93		1032			,
Hexane	3.90*	3.84		39.8	4,509,669		*
2-Hexanone <sup>d</sup>	1.38	1.36		22.6	7499		*
Methoxychlor	5.08	5.00		18.8			•
1-Methylnaphthalene	3.87*	3.81		135	33,728		
4-Methyl-2-pentanoned	1.31*	1.29		33,2	15,110		
2-Methylphenol <sup>d</sup>	1.99	1.96		11.8	445	1197	
Methylene chloride	1.25	1.23		375	18,407	7272	
Naphthalene	3.36	3.31		242	12,533	23,510	
2-Octanone <sup>d</sup>	2.378	2.33		17.8			
PCBs Aroclor® 1221	4.70 <sup>h</sup>	4.62		118	25,180		
Aroclor® 1232	5.10 <sup>h</sup>	5.02		602	128,683		
Aroclor® 1242	5.60 <sup>h</sup>	5.51		170	28,963		4.9
Aroclor® 1248	6.20 <sup>h</sup>	6.10		1014			
Aroclor® 1254	6.50 <sup>h</sup>	6.39		814		71,564	
Aroclor® 1260	6.80 <sup>th</sup>	6.69		4,574,333	<63,262		
Pentachlorobenzene	5.26	5.17		701			

Table 4. (continued)

					Lo	west Chronic Value	for:
Chemical	Log Kow <sup>b</sup>	Log Koc	NAWQC Chronic	Secondary Chronic Value	Fish	Daphnids	Non-Daphnid Invertebrates
1-Pentanol <sup>d</sup>	1.518	1.49		33.8	9361		
Phenanthrene	4.55	4.48	1800°			59,770	
Phenol	1.48	1.46	32		<57.4	· 575	
2-Propanoi <sup>d</sup>	0.05	0.05		0.084 5	6.65		,
1,1,2,2 Tetrachloroethane	2.39	2.35		1372	5400	22,274	•
Tetrachloroethene	2.67	2.63		416	3562	3180	•
Tetrachloromethane	2.73 <sup>r</sup>	2.69		1166			
Toluene	2.75	2.71	•	49.8	6449	128,218	•
Tribromomethane	2.35 <sup>f</sup>	2.31		658			
1,2,4-Trichlorobenzene	4.01	3.94		9683			
1,1,1-Trichloroethane	2.48	2.44		30.3	9635	4882	
1,1,2-Trichloroethane	2.05	2.02		1251	9797	19,176	
Trichloroethene	2.71	. 2.67		218	51,529	33,689	

Table 4. (continued)

					Lowest Chronic Value for:		
Chemical	Log Kow <sup>b</sup>	Log Koc	NAWQC Chronic	Secondary Chronic Value	Fish	Daphnids	Non-Daphnid Invertebrates
Vinyl acetate	0.73	0.72		0.840	42.5		
Xylene	3.13°	3.08		156	748,400		
m-Xylene	3.20	3.15		25.3			

#### Notes:

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b Log Kow values are from EPA (1995a), except where noted otherwise.

<sup>c</sup> Denotes proposed EPA sediment quality criteria.

d Denotes polar nonionic organic compounds, for which the EqP model is likely to provide a conservative estimate of exposure.

Most conservative (i.e., lowest) recommended value for reported configurations. BHC (other) is lowest of alpha-, beta-, and delta-BHC, only.

f Source is EPA (1995b).

Source is search of Syracuse Research Corporation, Environmental Sciences Center's on-line Experimental Log P Database conducted on June 7, 1996.

h Source is ATSDR (1989).

<sup>\*</sup> Conventional aqueous benchmarks are presented in Suter and Tsao (1996). EqP = equilibrium partioning. All sediment benchmarks are in  $\mu g/kg$  and are estimated assuming 1% TOC. Estimated sediment quality benchmarks greater than 10% (100,000,000  $\mu g/kg$ ) are not included because such concentrations are assumed to be exceedingly unlikely under natural conditions [applies to bis(2-ethylhexyl)phthalate and di-n-octylphthalate].

The available NOAA and FDEP values are presented in Table 5. An effort is underway to produce the same type of data base for freshwater sediments (MacDonald 1993). Freshwater SQBs should replace the marine and estuarine SQBs when they become available.

#### 3.3 SLC BENCHMARKS

The Ont. MOE has prepared provincial sediment quality guidelines (SQGs) using the SLC approach. These values are based on Ontario sediments and benthic species from a wide range of geographical areas within the province (Persaud et al. 1990). The lowest effect level (Low) is the level at which actual ecotoxic effects become apparent. The severe effect level (Severe) represents contaminant levels that could potentially eliminate most of the benthic organisms (Persaud et al. 1990). These "low" and "severe" effect values are potential SQBs and are presented in Table 5.

Although SLC derived values are based on biological effects and are suitable for all classes of chemicals and most types of sediment, the endpoint used to derive them (species absence) is considered insensitive (MacDonald 1994). Therefore, the SLC values may not be adequately protective. A qualitative comparison of the SLC values to the NOAA and FDEP values in Table 5 suggests that the Low values may be moderately under-protective for most organics. Nine of 10 Low values are approximately 2 to 10 times higher than the ER-L or TEL. However, the Low values for metals are remarkably similar to the ER-L or TEL values. Most of the Severe values for metals appear to be reasonably comparable to the ER-M or PEL, but many of the Severe values for organics are 10 to 100 times higher than the ER-M or PEL.

One advantage to the use of the MOE values for organic chemicals is that they are normalized to 1% TOC. Therefore, these SQBs can be adjusted for site-specific OC content similarly to the adjustment made for EqP SQBs.

#### 3.4 APPARENT EFFECTS THRESHOLDS

The AET is the sediment chemical concentration above which statistically significant biological effects always occur (EPA 1989b). Therefore, they may be under-protective because biological effects are observed at chemical concentrations well below AET values (Chapman 1989). AET values for several ionic and polar organic chemicals are retained in this revision because of the significant complexities associated with using the EqP approach.

Organic compounds that are polar or ionic include methyl and thiocarbamates, triazines, amines and analines, and organic acid pesticides (aliphatic and aromatic acids and esters, phenoxy compounds, and ureas). Unlike nonpolar and nonionic organic contaminants, both polar and ionic organic compounds may adsorb onto sediments by a variety of mechanisms, including hydrophobic interaction, nonspecific ion association, ion exchange, ion-dipole interactions, hydrogen bonding, and complex formation by surface metals (Shea 1988). It is possible that a multiple-term model might account for polar organic partitioning between sediment and aqueous phases, but such a model does not exist (Shea 1988).

The behavior of ionic organic pollutants has not been extensively studied. As with the nonionic organic chemicals, OC appears to be a critical factor in the partitioning behavior in sediments (Jafvert 1990). The critical micelle concentration (Di Toro et al. 1990) and pH (Jafvert 1990) also appear to be dominating factors.

Table 5. Summary of selected integrative and screening level concentration-based sediment quality benchmarks  $^a$ 

	NOA	A <sup>b</sup>	FDF	EP <sup>c</sup>	Ont. MOE		
Chemical	ER-L	ER-M	TEL	PEL	Low	Severe	
		Inorganics (					
Antimony	2 <sup>e</sup>	25 <sup>e</sup>					
Arsenic	8.2	70	7.24	41.6	6	33	
Cadmium	1.2	9.6	0.68	4.21	0.6	10	
Chromium	81	370	52.3	160	26	110	
Copper	34	270	18.7	108	16	110	
Iron					2%	4%	
Lead	46.7	218	30.2	112	31	250	
Manganese					460	1110	
Mercury	0.15	0.71	0.13	0.7	0.2	2	
Nickel	20.9	51.6	15.9	42.8	16	75	
Silver	1.0	3.7	0.73	1.77			
Zinc	150	410	124	271	120	820	
		Organics (	μg/kg dry weig	ht)			
Acenaphthene	16	500	6.71	88.9			
Acenaphthylene	44	640	5.87	128			
Aldrin					2	80	
Anthracene	85.3	1100	46.9	245			
Benz(a)anthracene	261	1600	74.8	693			
Benzo(a)pyrene	430	1600	88.8	763			
ВНС					3	120	
BHC, alpha-					6	100	
BHC, beta-					5	210	
Bis(2- ethylhexyl)phthalate			182	2647 -			
Chlordane	0.5 <sup>e</sup>	6 <sup>e</sup>	2.26	4.79	7	60	
Chrysene	384	2800	108	846			
DDD, o,p'-+ p,p'-	2 <sup>e</sup>	20°					
DDD, p,p'-	-	<del></del>	1.22	7.81	8	60	
DDE, p,p'-	2.2	27	2.07	3.74	5	190	
DDT, o,p'-+p,p'-	1°	7°	2.07	• • • • • • • • • • • • • • • • • • • •	8	710	
	•	•	1.19	4.77	_		
DDT, p,p'- DDT, Total <sup>f</sup>	1.58	46.1	3.89	51.7	7	120	
· ·	63.4	260	6.22	135	•		
Dibenzo(a,h)anthracene	0.02 <sup>e</sup>	200 8 <sup>e</sup>	0.72	4.3	2	910	
Dieldrin		8 45 <sup>e</sup>	0.12	٠.٦	3	1300	
Endrin	0.02		112	1494	,	1500	
Fluoranthene	600	5100	113				
Fluorene	19	540	21.2	144	5 <sup>g</sup>	50	
Heptachlor epoxide					5° 3 <sup>g,i</sup>	50 10 <sup>h</sup>	
Lindane (gamma-BHC)			0.32	0.99	3°°	10"	
2-Methyl naphthalene	70	670	20.2	201			
Mirex					7	13	

20 Table 5. (continued)

	NOAAb .		, FI	DEP <sup>c</sup>	Ont. MOE <sup>d</sup>	
Chemical	ER-L	ER-M	TEL	PEL	Low	Severe
Naphthalene	160	2100	34.6	391		
PAH, Total LMW	552	3160	312	1442		
PAH, Total HMW <sup>J</sup>	1700	9600	655	6676		
PAH, Total	4022	44792	1684	16770	2000	110,000
PCB, Total	22.7	180	21.6	189	70 <sup>1</sup>	5300 <sup>1</sup>
PCB, 1016					7 <sup>8.1</sup>	530 <sup>h,l</sup>
PCB, 1248					30 <sup>g,1</sup>	1500 <sup>h,i</sup>
PCB, 1254					60 <sup>g.</sup>	340 <sup>h,i</sup>
PCB, 1260					5 <sup>g,1</sup>	240 <sup>h.i</sup>
Phenanthrene	240	1500	86.7	544		
Рутепе	665	2600	153	1398		

<sup>a</sup> Benchmark values are presented herein with the same number of significant digits used in the source document.

NOAA = National Oceanic and Atmospheric Administration; ER-L = effects range-low; ER-M = effects range-median; except where noted, effects levels are the updated and revised values from Long et al. (1995).

FDEP = Florida Department of Environmental Protection; TEL = threshold effects level; PEL = probable effects level; source

document is MacDonald (1994).

Source document is Long and Morgan (1991).

Denotes tentative guideline.

d Ont. MOE = Ontario Ministry of the Environment; Low = lowest effect level and is the 5th percentile of the screening level concentration, except where noted otherwise; Severe = severe effect level and is the 95th percentile of the screening level concentration, except where noted otherwise; source document is Persaud et al. (1990); values for organic chemicals were normalized assuming one percent total organic carbon.

Total DDT is the sum of the concentrations of the o,p'- and p,p'- isomers of DDD, DDE, and DDT.

<sup>10</sup>th percentile of the screening level concentration.

<sup>90</sup>th percentile of the screening level concentration.

LMW = low molecular weight and is the sum of the concentrations of acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, and phenanthrene; HMW = high molecular weight and is the sum of the concentrations of benz(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, and pyrene; Total is the sum of the concentrations of the aforementioned low and high molecular weight PAHs.

The state of Washington has developed sediment quality standards for some polar and ionic organic compounds (Table 6). AETs are site-specific and should be used cautiously. Because little information is available for ionic organics, these contaminants should not be eliminated in a screening risk assessment. Preliminary comparisons can be made to the Washington State sediment quality standards to give an indication of the magnitude of the contamination. In addition, EqP SQBs for two of the polar chemicals (2-methylphenol and phenol) are presented in Table 4.

WQBs do exist for several of these chemicals (Suter and Tsao 1996). If pore water concentrations of these chemicals are available, they should be screened against those benchmarks; this was the methodology followed in the Phase I Screening Ecological Risk Assessment for the Clinch River (Cook et al. 1992).

#### 3.5 ECOTOX THRESHOLDS

EPA's OSWER has published Ecotox Thresholds (ETs) which are intended to be used for screening contaminants at CERCLA sites (OSWER 1996). These values are available for 8 metals and 41 organics in sediments and are presented in Table 7; their derivation is briefly explained herein.

The preferred method for determining sediment ETs is to use the proposed SQC values (EPA 1993a to e), which are derived using the equilibrium partitioning method. Superfund has elected to use the lower limit of the 95% confidence interval as the ET, rather than the central tendency value, to maintain an appropriate level of conservatism for screening purposes (OSWER 1996). The SQC ETs in Table 7 are normalized to 1% TOC.

SQBs are used when SQCs are not available. The SQB is calculated in the same manner as the SQC except that a Tier II Secondary Chronic Value is used. Four of these are from the Great Lakes Water Quality Initiative (EPA 1992), 12 are from Suter and Mabrey (1994), and 17 were calculated by OSWER (1996). Three chemicals with OSWER-derived SCVs (endosulfan, methoxyclor, and malathion) had NAWQCs, but the criteria were judged to be old and unreliable. Tier II values were not derived if no daphnia acute values were available. The SQB ETs in Table 7 are normalized to 1% TOC.

The ER-L value is used if neither an SQC nor an SQB was available. OSWER noted that there is relatively low correlation between the incidence of effects and the ER-Ls for mercury, nickel, total PCBs, and DDT (Long et al. 1995) and that the ETs for these four chemicals should be used cautiously.

#### 3.6 REGION IV SCREENING VALUES

EPA Region IV has published ecological screening values (SVs) for sediments (Region IV 1995). They are presented in Table 7. The selected effect level is the lower of the ER-L (Long et al. 1995) and TEL (MacDonald 1994). The ER-L for antimony is from Long and Morgan (1990). When the Contract Laboratory Program's Practical Quantitation Limit (PQL) is above the effect level, the screening value defaults to the PQL. However, if concentrations below the PQL are reported, they should be compared to the effect level.

Table 6. Washington State sediment quality standards for ionizable organic compounds (micrograms per kilogram dry weight)

Compound	Washington State sediment quality standard
Benzoic acid	650
Benzyl alcohol	57
Pentachlorophenol	360
Phenol	420
2-Methyl phenol	63
4-Methyl phenol	670
2,4-Dimethyl phenol	29

Source: Ginn, T. C., and R. A. Pastorak. 1992. Assessment and Management of Contaminated Sediments in Puget Sound. pp. 371-401 in Sediment Toxicity Assessment, G. A. Burton, Jr. (eds.). Lewis Publishers, Boca Raton, Fla.

Table 7. EPA Region IV and OSWER sediment screening values<sup>a</sup>

	Reg IV⁵		OSWER	
Chemical	Value	Type <sup>d</sup>	Value	Type <sup>e</sup>
	Inorganics (mg/kg	dry weight)		
Antimony	12	ER-L <sup>f</sup>		
Arsenic	7.24	TEL	8.2	ER-L
Cadmium	1	PQL	1.2	ER-L
Chromium	52.3	TEL	81	ER-L
Copper	18.7	TEL	34	ER-L
Lead	30.2	TEL	47	ER-L
Mercury	0.13	TEL	0.15	ER-L
Nickel	15.9	TEL	21	ER-L
Silver	2	PQL		
Zinc	124	TEL	150	ER-L
	Organics (ug/kg d	ry weight)		
Acenaphthene	330	PQL	. 620	SQC
Acenaphthylene	330	PQL		
Anthracene	330	PQL		
Benzene			57	SQB
Benzo(a)anthracene	330	PQL		

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Table 7. (continued)

	Reg l	V <sup>b</sup>	OSWER	
· Chemical	Value	Typed	Value	Type
Benzo(a)pyrene	330	PQL	430	ER-L
Biphenyl			1100	SQB
Bis(2-ethylhexyl)phthalate	182	TEL		
4-Bromophenyl phenyl ether			1300	SQB
Butylbenzyl phthalate			11,000	SQB
Chlordane	3.3	PQL		
Chlorobenzene			820	SQB
Chrysene	330	PQL		
DDD	3.3	PQL		
DDD, p,p'-	3.3	PQL		
DDE	3.3	PQL		
DDT	3.3	PQL		
DDT, p,p'-	3.3	PQL		
DDT, Total <sup>g</sup>	3.3	PQL	1.6	ER-L
Diazinon			1.9	SQB
Dibenzofuran			2000	SQB
Dibenzo(a,h)anthracene	330	PQL		
1,2-Dichlorobenzene			340	SQB
1,3-Dichlorobenzene			1700	SQB
1,4-Dichlorobenzene			350	SQB
Dieldrin	3.3	PQL	52	SQC
Diethyl phthalate			630	SQB
Di-n-butylphthalate			11,000	SQB
Endosulfan, mixed isomers			5.4	SQB
Endosulfan, alpha-			2.9	SQB
Endosulfan, beta-			14	SQB
Endrin	3.3	PQL	20	sqc
Ethylbenzene			3600	SQB
Fluoranthene	330	PQL	2900	SQC
Fluorene	330	PQL		
Hexachloroethane			1000	SQB
Lindane (gamma HCH)	3.3	PQL	3.7	SQB
Malathion		•	0.67	SQB

24 Table 7. (continued)

Chemical	Reg	OSWER		
	Value	Type <sup>d</sup>	Value	Туре
Methoxychlor			19	SQB
2-Methylene naphthalene	330	PQL		
Naphthalene	330	PQL	480	SQB
PAHs, Total LMWh	330	PQL		
PAHs, Total HMWh	655	TEL		
PAHs, Total <sup>h</sup>	1684	TEL	4000	ER-L
PCBs, Total			23	ER-L
Phenanthrene	330	PQL	850	sqc
Pyrene	330	PQL	660	ER-L
1,1,2,2-Tetrachloroethane			940	SQB
Tetrachloroethylene			530	SQB
Tetrachloromethane			1200	SQB
Toluene			670	SQB
Toxaphene			28	SQB
Tribromomethane			650	SQB
1,2,4-Trichlorobenzene			9200	SQB
1,1,1-Trichloroethane			170	SQB
Trichloroethylene			1600	SQB
m-Xylene			25	SQB

<sup>\*</sup> Screening values are presented herein with the same number of significant digits used in the EPA source documents.

b Reg IV = EPA Region IV ecological screening values for sediments (Region IV 1995) and is either the selected sediment effects value or the PQL, whichever is greater. The selected effects value is the lower of the ER-L and TEL.

<sup>&</sup>lt;sup>e</sup> OSWER = EPA Office of Solid Waste and Emergency Response Ecotox Thresholds (ET). Only the most preferred ET, as defined in OSWER (1996), is presented.

<sup>&</sup>lt;sup>d</sup> ER-L = effects range-low and, except where noted otherwise, is from Long et al. (1995); TEL = threshold effects level and is from MacDonald (1994); PQL = Contract Laboratory Program's practical quantification limit.

ER-L = is the same as for Reg IV values; SQC = the lower limit of the 95 percent confidence interval of the proposed EPA sediment quality criteria, assuming one percent total organic carbon; SQB = the EPA sediment quality benchmark based EPA Teir II Chronic value (Region IV 1996), assuming one percent total organic carbon.

f Value is from Long and Morgan (1991).

E Total DDT is the sum of the concentrations of the 0,p'- and p,p'- isomers of DDD, DDE, and DDT.

h LMW = low molecular weight and is the sum of the concentrations of acenaphthene, acenaphthylene, anthracene, fluorene, 2-methylnaphthalene, naphthalene, and phenanthrene; HMW = high molecular weight and is the sum of the concentrations of benz(a)anthracene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, fluoranthene, and pyrene; Total is the sum of the concentrations of the aforementioned low and high molecular weight PAHs.

#### 3.7 BACKGROUND CONCENTRATIONS

Background sediment concentrations should be used as a check for the metals benchmarks. That is, because some of these benchmarks are quite conservative and because the measured concentrations in ambient sediment may include forms that are not bioavailable, benchmark concentrations may be lower than background sediment concentrations. If the background concentrations are valid and represent an uncontaminated state and if the exposure site does not contain forms of the chemicals that are more bioavailable or toxic than the forms at background sites, then screening benchmarks lower than the background concentration should not be used.

### 4. BENCHMARK USE IN BASELINE ECOLOGICAL RISK ASSESSMENTS

To evaluate ecological effects of contaminated sediments for a baseline ERA, it is recommended that sediment be collected for toxicity testing, and the benthic macroinvertebrate community be surveyed. This is important because chemical concentrations are not accurate predictors of biological and ecological effects. This is because the percentage of the chemical that is bioavailable may range from 0 to 100% (Burton and Scott 1992). Benchmarks may be used to determine which chemicals present in the sediment are most likely causing the toxicity. Use of a weight-of-evidence approach enables a more accurate evaluation of adverse ecological impact.

ASTM has approved standard methods for conducting whole-sediment toxicity tests with the freshwater invertebrates *Hyalella azteca* (an amphipod) and *Chironomus tentans* and *C. riparius* (both midges) (Ingersoll and Nelson 1990) and with zooplankton *Daphnia* sp. and *Ceriodaphnia* sp. (both cladocerans). A draft method exists for the burrowing mayfly *Hexagenia limbata* (Burton and Scott 1992). Based on a number of sediment contamination studies, the most consistently efficient indicators of acute and short-term chronic toxicity in whole sediments are these aforementioned organisms (Burton and Scott 1992).

A separate technical memorandum will be produced that outlines the toxicity test methods recommended for ERA at the ORR and the Portsmouth and Paducah Gaseous Diffusion plants.

#### 5. CHEMICAL-SPECIFIC CONSIDERATIONS

Sections 2 and 3 address the general considerations associated with using sediment benchmarks to evaluate the various chemical types (e.g., metals, nonionic organics, polar organics, and ionic organics). The following text addresses chemical-specific information that should be considered when using these benchmarks, with a focus on the reliability of a benchmark for a given chemical. The chemical-specific considerations associated with WQBs used in the EqP SQBs are discussed in Suter and Tsao (1996). A chemical-by-chemical evaluation of the Ont. MOE values was not available (Persaud et al. 1990). However, MacDonald (1994) and Long et al. (1995) did discuss the degree of reliability associated with the NOAA and FDEP values for each chemical.

Reliability is a function of the agreement between the predicted and observed incidence of effects, as discussed in MacDonald (1994) and Long et al. (1995). Reliability of the TEL is low if >25% of the concentrations below the TEL were associated with effects (i.e., the number of "hits" below the TEL divided by the total number of concentrations below the TEL is >0.25). Based on this criterion, a TEL with low reliability may be under-protective, and caution should be used when attempting to

exclude that chemical as a chemical of potential ecological concern. Reliability of the PEL is low if <50% of the concentrions above the PEL were associated with effects. Therefore, a PEL with low reliability may overpredict the potential for real effects; this is primarily of concern when the SQBs are used in baseline assessments to help predict the magnitude of effects and help determine causality of observed effects.

The designations by Long et al. (1995) (relatively high reliability and lower reliability) were somewhat different than the designations by MacDonald (1994) (low, moderate, and high). The designation of low reliability also is used herein for the ER-Ls and ER-Ms, because SQBs of low reliability are of particular concern. Reliability is considered low if the incidence of effects is >25% at concentrations below the ER-L. Reliability of the ER-M is considered low if the incidence of effects is <50% at concentrations above the ER-M. Other factors (e.g., concordance of effects) also were considered by MacDonald (1994) and Long et al. (1995) to determine the overall reliability of the FDEP and NOAA values, respectively. These determinations also are presented in the following text, where appropriate.

#### **5.1 METALS**

- Antimony—Data are available from only two geographic regions (Puget Sound/Commencement Bay and San Francisco Bay); therefore, the degree of confidence in the NOAA values is moderate (Long and Morgan 1991). No criteria are available for comparison from FDEP or Ontario MOE.
- Arsenic—Confidence in the TEL and ER-L is high and relatively high, respectively. Confidence in the ER-M is somewhat lower, and confidence in the PEL is Low. Therefore, the TEL and ER-L appear to be reliable indicators of the threshold for effects, and the ER-M appears to be the better indicator of the level above which real effects are likely.
- Cadmium—A relatively large amount of data exists for cadmium including spiked-sediment toxicity tests and EqP-based assessments (MacDonald et al. 1994). Klapow and Lewis (1979) calculated a statistically significant difference in the medians of acute aqueous toxicity data from saltwater and freshwater organisms. This supports the findings of Eisler (1985) (Long and Morgan 1991), who found resistance to cadmium higher among marine than freshwater species. However, the degree of confidence in the lower and upper NOAA and FDEP values is high, and these values are considered to be reliable predictors of effects.
- Chromium—There are some inconsistencies in the data available for chromium, possibly due to lack of speciation information. All data were reported as total chromium, whereas the hexavalent form is more toxic than the trivalent form. There also are no supporting data from single-chemical spiked-sediment toxicity tests or from the EqP approach (MacDonald et al. 1994). Overall confidence in the FDEP values, and the PEL in particular, is moderate. Although the overall confidence in the NOAA values is relatively high, Long et al. (1995) cautioned that the incidence of effects may be unduly exaggerated by data from multiple tests performed in only two studies. Based on the available evaluations, the TEL and ER-L appear to be reliable predictors of the threshold for effects.
- Copper—Considerable data exist for copper in sediments, and a relatively high degree of overall confidence exists for the NOAA values. Overall confidence in the FDEP values, and the PEL in particular, is moderate only. However, the TEL is considered to be a highly reliable predictor of the threshold for effects.

- Iron—The only available benchmarks are the Ont. MOE Low and Severe effect levels. Although the reliability of these data was not addressed (Persaud et al. 1990), the Ont. MOE guidelines were derived for freshwater sediments. Therefore, these values appear to warrant a moderate degree of confidence.
- Lead—Considerable data exist for lead in sediments, and a relatively high degree of overall confidence exists for the NOAA values. Overall confidence in the FDEP values, and the PEL in particular, is moderate only. However, the TEL is considered to be a reliable predictor of the threshold for effects. This is consistent with expected reliability of the ER-L and ER-M values. Although a relatively large amount of data exist for lead, there were no spiked-sediment toxicity test data to confirm the toxic concentrations (MacDonald et al. 1994).
- Manganese—The only available benchmarks are the Ont. MOE Low and Severe effect levels. Although the reliability of these data was not addressed (Persaud et al. 1990), the Ont. MOE guidelines were derived for freshwater sediments. Therefore, these values appear to warrant a moderate degree of confidence.
- Mercury—Considerable data exist for mercury, though only total mercury concentrations were reported in the data set (MacDonald et al. 1994). Confidence in the TEL and ER-L is high and relatively high, respectively. Therefore, the lower screening values should beat least conservative predictors of the threshold for effects. The PEL and ER-M may significantly overpredict the likelihood of real effects, given that confidence in these values is Low. In addition, the overall confidence in the FDEP values is low.
- Nickel—Toxicity of nickel is greatly influenced by water hardness and salinity (Long and Morgan 1991). Data were from marine and estuarine field studies only, and no spiked-sediment toxicity tests or EqP approaches were used (MacDonald et al. 1994). Confidence in the TEL and ER-L is high and relatively high, respectively. Therefore, the lower screening values should be at least conservative predictors of the threshold for effects. The PEL and ER-M may significantly overpredict the likelihood of real effects, given that confidence in these values is Low.
- Silver—A moderate amount of data is available for silver in sediments, though there are no data from spiked-sediment toxicity tests or from EqP approaches (MacDonald et al. 1994). The FDEP and NOAA values hold moderate and relatively high overall confidence, respectively. These data suggest that the ER-L and TEL are likely to be reliable predictors of the threshold for effects. The ER-M is likely to be a better predictor of real effects because confidence in the PEL is Low.
- Zinc—Considerable data exist for zinc in sediments including spiked-sediment toxicity tests and EqP-based assessments (MacDonald et al. 1994). Overall confidence in the FDEP values, and the PEL in particular, is moderate only. However, the TEL is considered to be a reliable predictor of the threshold for effects. This is consistent with expected reliability of the NOAA values.

#### **5.2 ORGANICS**

Polycyclic aromatic Hydrocarbons (PAHs)—The reliability of the individual TELs and PELs ranged from moderate to high, as did overall reliability of the FDEP values. The TELs and PELs may be somewhat overprotective for four PAHs [i.e., acenaphthene, acenaphthylene, fluorene, benz(a)anthracene, dibenzo(a,h)anthracene, and total high molecular weight polyaromatic hydrocarbons] for which the overall FDEP or ER-M values are considered moderately reliable.

The TELs for fluorene and dibenzo(a,h)anthracene are considered to be only moderately reliable predictors of the threshold for effects. The TELs and PELs should be reasonably reliable predictors of the likelihood of effects for the remaining PAHs. Reliability of the ER-Ls for anthracene and fluorene is low, while reliability of the ER-M for dibenzo(a,h)anthracene is relatively low. The reliability of the ER-Ls and ER-Ms for the remaining PAHs is relatively high.

Total Polychlorinated Biphenyls (PCBs)—The overall reliability of the FDEP values was low, and the reliability of the TEL and PEL was only moderate. Reliability of the ER-M is considered to be relatively low. Concordance of the concentrations and effects was not high for either the NOAA or FDEP values. This may be the result of insufficiently detailed chemical information. That is, the mixture of PCB congeners may have varied considerably among sites and studies, but this information was unavailable or not included in the NOAA and FDEP analyses. Caution should be used when screening PCBs with these benchmarks.

Pesticides—The overall reliability of the FDEP values was low for chlordane, total DDT, and lindane and moderate for dieldrin and the p,p' isomers of DDD, DDE, and DDT. The TEL for total DDT is considered to have low reliability and is likely to be a poor predictor of the threshold for effects. The PELs for chlordane, p,p'-DDD, and lindane are considered to have low reliability and are likely to overpredict the likelihood of real effects. This is also somewhat true of the PELs for the other four pesticides. NOAA values are available for only two pesticides, p,p'-DDE and total DDT, for which poor concordance of effects and concentrations was observed. This may be due to the inclusion of relatively low EqP values which were not based on toxicity to benthic organisms (Long et al. 1995). Therefore, the NOAA values may tend to overpredict the likelihood of effects.

Bis(2-ethylhexyl)phthalate—The overall reliability of the FDEP values was high, as was the reliability of the TEL and PEL. These values are expected to be reliable predictors of the likelihood of effects. NOAA values are not available for bis(2-ethylhexyl)phthalate.

#### 6. UNCERTAINTIES/LIMITATIONS

The EqP methodology has several uncertainties. It relies on an empirical model to compute the pore water concentration from the solid phase measurements. Therefore, there is an uncertainty associated with the use of the model. In addition, uncertainty exists with respect to the  $K_{ow}$  associated with the specific chemical because it is an experimentally determined quantity (EPA 1989a). Various types of organic matter present in sediments can have significantly different binding capacities for organic contaminants; the affinity depends in large part on the source and nature of the carbon. For example, organics associated with sediments contaminated with petroleum hydrocarbons would tend to be much less toxic than those associated with sediments whose OC is natural OC (Lee and Jones-Lee 1993).

The assumption that benthic organisms have similar sensitivities to water column species has a level of uncertainty (EPA 1993f). This may be of particular concern for tube-dwelling amphipods. The tubes tend to isolate them from the interstitial water, causing speculation that their exposure is at the sediment/water interface. Additionally, the amphipod tubes are matrices of organics and inorganics; the tube walls could sorb appreciable amounts of organic contaminants, which could alter the availability of sediment-associated contaminants to those organisms (Lee and Jones-Lee 1993).

The EqP approach is known not to work for all nonpolar organics.. It is well known that many pesticides that are sorbed onto soils and sediments are in the form of "bound" pesticide residues that do not participate in equilibrium reactions with water (Lee and Jones-Lee 1993).

The aquatic benchmarks [EPA WQC for the protection of aquatic life and the aquatic benchmarks developed by Suter and Tsao (1996)] for polychlorinated biphenyls and several polynuclear aromatic hydrocarbons are class criteria based on the cumulative concentration of all members of the class. In the derivation of sediment benchmarks using the EqP approach and the aquatic benchmarks, it is necessary to apply the class level to each member of the class individually because each has a unique  $K_{oc}$  (Lake et al. 1990). In environments where one class member comprises the majority of the sediment burden of the class, this approach should be adequate. However, if numerous class constituents are significantly enriched, a safe threshold for the class as a whole may be exceeded even though no individual constituent violates its predicted safe level (based on the aquatic benchmark) (Pavlou 1987).

The Washington State AET, NOAA, and FDEP values have several limitations. Primarily, all or most of the data used in their derivation were based on marine and estuarine systems. These values are being applied to freshwater systems at the ORR and the Portsmouth and Paducah Gaseous Diffusion plants. Differences include physico-chemical characteristics of the system as well as possible differences in sensitivity of biota. Washington State, NOAA, and FDEP values are for single chemicals, although sediments containing chemical mixtures were used for their derivation. The Ont. MOE values were derived to be applicable to sediment types throughout the province of Ontario. The differences between Ontario and east Tennessee, Ohio, and Kentucky sediments and biota introduce a level of uncertainty.

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- 53. D. Gonzales, Jacobs Engineering, 125 Broadway, Oak Ridge, TN 37830
- 54. G. Snyder, Jacobs, Engineering, 100 West 3rd St., Piketon, OH 45611
- 55. J. Tate, Jacobs, Engineering, 125 Broadway, Oak Ridge, TN 37830
- 56. D. Wilkes, Jacobs, Engineering, 175 Freedom Blvd., Kevil, KY 42053
- 57. P. Carter, Science Applications International Corporation, 11197 U.S. Route 23, Suite 200, Waverly, Ohio 45690
- B. Kornaby, Science Applications International Corporation, P.O. Box 2501, 301, Laboratory Rd., Oak Ridge, TN 37831
- S. Pack, Science Applications International Corporation, P.O. Box 2501, 301, Laboratory Rd., Oak Ridge, TN 37831
- 60. B. G. Blaylock, SENES, 102 Donner Drive, Oak Ridge, TN 37831
- 61. K. Hopper, Systematic Management Services, 117 Broadway Ave., Oak Ridge, TN 37830